

# Phosphorus Solubility in Response to Acidification of Dairy Manure Amended Soils

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Manure additions beyond crop P needs result in accumulated soil Ca phosphate (Ca-P). Although stable near neutral pH levels, there is concern about the solubility of accumulated soil Ca-P when soil pH conditions become acidic, potentially releasing water-soluble P (WSP). The purpose of this study was to examine changes in WSP among non-acidic, Ca-P-accumulated soils in response to six levels of acidification and acidification timing. Two soils that historically received excessive dairy manure were incubated for 8 wk with pH adjusted by single-point or gradual acid additions. After 8 wk, acid additions ceased and WSP, Mehlich-3 P (M3-P), and pH were determined before continuing the incubation for two additional weeks. Soil pH had little effect on M3-P, while acidification timing interacted with the effect of pH on WSP concentrations. After 8 wk, single-point acidification resulted in WSP decreases with decreasing pH, but gradual acidification showed the opposite effect in the pH range 4.5 to 6.5. This effect disappeared after two additional weeks of incubation, resulting in overall decreased WSP concentrations. Results suggested that among the high-P (Ca-P) soils used in this study, which contained significant Fe and Al, acidification did not increase WSP beyond the original concentrations since dissolved Ca-P was resorbed onto soil Fe and Al. This subsequent resorption of P was not immediate, however, and was dependent on kinetics. Overall decreases in soil WSP resulting from acidification is beneficial to water quality through prevention of nonpoint dissolved P losses from soils to surface waters.

Abbreviations: Ca-P, calcium phosphate; M3-P, Mehlich-3 extractable phosphorus; WSP, water-soluble phosphorus.

INCREASED P CONCENTRATIONS in surface waters can contribute to algal blooms and subsequent eutrophication, resulting in the depletion of O<sub>2</sub> and potential fish kills (Correll, 1998; Foy and Withers, 1995). Excessive soil P concentrations have been linked to surface water quality degradation in economically important watersheds such as Chesapeake Bay and the Eucha-Spavina of Arkansas and Oklahoma, with agricultural soils identified as significant P sources

(Carpenter et al., 1998; Daniel et al., 1994). Many high-P soils occur in areas of concentrated animal agriculture and are a result of continuous manure applications based on crop N requirements that have resulted in P applications beyond plant requirements and subsequent P accumulation (Sims et al., 2002). Although P losses from agricultural soils are typically reduced with erosion control measures, soils with increased P concentrations can still potentially contribute significant soluble P loads even when erosion is minimal (Vadas et al., 2005).

Often animal manures are typically high in various types of calcium phosphates (Ca-P). The presence of calcium phosphates (octocalcium phosphate, dicalcium phosphate) in liquid cattle manures was identified in a study by Fordham and Schwertmann (1977). Among a comparison of different biosolids and poultry litter, Penn and Sims (2002) found that 19% of poultry litter total P was in the form of Ca-P. Dou et al. (2003) showed that dairy, swine, and poultry litter samples consisted of 3, 30, and 41% HCl-extractable P (i.e., Ca-P), respectively, using the Hedley P fractionation scheme. Kalbasi and Karthikeyan (2004) showed that dairy manure had a Ca/P molar ratio of 2.73, suggesting significant manure Ca-P concentrations. In a survey of water-soluble P (WSP) among 140 livestock manure samples (beef, dairy, broilers, layers, swine, and turkey), Kleinman et al. (2005) found that WSP was significantly and positively correlated with water-soluble Ca in dairy cattle and swine manures, also suggesting a Ca-P form.

As expected, the continuous addition of Ca-P-rich manures to soils can lead to the accumulation of soil Ca-P (Nair et al., 1995; Beauchemin et al., 2003; Josan et al., 2005; Sato et al., 2005; Penn and Bryant, 2006a). For example, Sharpley et al. (2004) determined that among soils from 20 different sites (Oklahoma, New York, and Pennsylvania), those that received regular manure applications (swine, dairy, or poultry) were significantly higher in Ca-P than unamended soils, as estimated by sequential fractionation and speciation modeling. Sato et al. (2005) identified Ca-P as the dominant P form in poultry manure and long-term poultry-amended soils (compared with unamended soils) using x-ray absorption near-edge structure spectroscopy and sequential fractionation.

High concentrations of Ca-P in soils can have a profound effect on P solubility and thus the potential for nonpoint-source losses of dissolved P in runoff. Solubility of Ca-P is lowest at near-neutral pH. For example, brushite, monetite, octacalcium phosphate, tricalcium phosphate, and hydroxyapatite show minimum solubility and have sharp changes in P solubility occurring at pH 7 to 8 when the soluble Ca concentration is 10<sup>-2.5</sup> mol L<sup>-1</sup> or is fixed by calcite; the pH of this minimum solubility point will decrease with increasing Ca concentration. Solubility increases with increasing pH as CaCO<sub>3</sub> begins to precipitate, thereby removing Ca from solution (Lindsay, 1979). Solubility also increases as soils become more acidic. Therefore, the stability of insoluble forms of soil Ca-P is mainly a function of soil pH. In their study of poultry-manure-amended soils, Sato et al. (2005) suggested that acidification of Ca-P-dominated soils would increase P solubility (due to the dissolution of Ca-P), thereby increasing the risk of P leaching or loss in runoff. Since noncalcareous agricultural soils in humid leaching environments naturally acidify when pH is not maintained through lime or manure additions, the maintenance of soil pH becomes an important issue among high-Ca-P soils in regard to water quality. The objective of this study was to determine how the

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degree and timing of acidification affects P solubility among high-P soils that previously received large amounts of dairy manure.

## MATERIALS AND METHODS

### Soil Collection and Characterization

Soils 1 and 2 originated from two different dairy farms located in Lancaster County, Pennsylvania, representative of high animal intensity production on a restricted land base. These sites were described in a rainfall simulation study by Penn and Bryant (2006b). Both soils were a Lindside silt loam (fine-silty, mixed, mesic Fluvaquentic Eutrochrepts), sampled at the top 5 cm for initial characterization and used in incubation studies (described below). Both soils were air dried and sieved (2 mm) before characterization. Each site was located between a barn and a stream and historically received a very high amount of animal traffic and manure deposits as animals were fed or moved to pasture through this area.

Background characterization included the following: Water extraction of P was conducted by shaking 2 g of air-dried soil with 20 mL of deionized (DI) water end over end for 1 h, followed by centrifuging (2500 rpm for 5 min) and filtering with 0.45- $\mu$ m membranes. Background soil Mehlich-3 P (M3-P), Ca, Mg, and K concentrations were determined on soils from each site by shaking 2 g of air-dried soil with 20 mL of Mehlich 3 solution (0.2 mol L<sup>-1</sup> CH<sub>3</sub>COOH + 0.25 mol L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> + 0.015 mol L<sup>-1</sup> NH<sub>4</sub>F + 0.13 mol L<sup>-1</sup> HNO<sub>3</sub> + 0.001 mol L<sup>-1</sup> ethylenediamine tetraacetic acid [EDTA]) end over end for 5 min followed by filtration with Whatman no. 1 paper (Mehlich, 1984). Background soil ammonium oxalate P, along with Al and Fe (Al<sub>ox</sub> and Fe<sub>ox</sub>, respectively) concentrations were measured on soils from each site using a 1:40 ratio of soil to 0.2 mol L<sup>-1</sup> ammonium oxalate (pH 3), 2-h reaction time in the dark, and filtration with Whatman no. 42 paper (McKeague and Day, 1966). The ratio of ammonium oxalate extractable P to (Al + Fe), referred to as the degree of P saturation (DPS<sub>ox</sub>), was expressed as:

$$\frac{P}{(Al+Fe)\alpha}$$

with all values in millimoles per kilogram. The empirical constant  $\alpha$  is used to relate soil P sorption capacity to Al<sub>ox</sub> and Fe<sub>ox</sub> and the denominator acts to express the effective total soil P sorption maximum. For the sake of comparison to other studies, we assumed an  $\alpha$  value of 0.5 (Pautler and Sims, 2000; Sims et al., 2002). The ratio of Mehlich-3 P to (Al + Fe) was determined in the same manner, but without the use of the empirical constant, as recommended by Sims et al. (2002). This is referred to as Mehlich-3 degree of P saturation (DPS<sub>M3</sub>). All Ca, Mg, K, P, Al, and Fe in the extracts were measured with inductively coupled plasma atomic emission spectroscopy (ICP-AES). Soil pH was measured in a 1:1 soil/DI water slurry using a pH electrode. Sand, silt, and clay contents were estimated by the hydrometer method (Day, 1965) and organic matter was estimated by loss-on-ignition (Nelson and Sommers, 1996). Cation exchange capacity was determined at pH 7 by the ammonium saturation method (Sumner and Miller, 1996).

In addition, P forms were identified and estimated for the two unincubated soils by use of chemical speciation modeling and a sequential P chemical fractionation. Saturated paste water extractions were conducted in triplicate at a 1:5 soil/DI water ratio, shaking end over end for 16 h, followed by centrifuging (2500 rpm for 5 min) and filtering with 0.45- $\mu$ m membranes. All extracts were analyzed for P, K, Ca, Mg, Al, and Fe by ICP-AES. Solution pH and ionic strength (as

estimated by electrical conductivity [Griffin and Jurinak, 1973]) was also measured on each water extract. The data from the water extracts were used to predict the presence of solid mineral phases in the original samples as determined by the MINTEQA2 speciation model (Allison et al., 1991). Soil P was fractionated in triplicate according to the procedure of Hedley et al. (1982). This involved sequentially extracting P from 1 g of soil with 30 mL of DI water, 30 mL of 0.5 mol L<sup>-1</sup> of NaHCO<sub>3</sub> (pH 8.5), 30 mL of 0.1 mol L<sup>-1</sup> NaOH, and 30 mL of 1 mol L<sup>-1</sup> HCl. Between each fractionation step, extracts were centrifuged (2500 rpm for 10 min) to separate the soil from the extracting solution, which was then filtered through Whatman no. 42 paper. All solutions were analyzed for P by ICP-AES.

### Acid-Amended Soil Incubation

Soil pH buffer curves were established by the titration method. This involved adding 1 mL of 0.5 mol L<sup>-1</sup> HCl every 20 min to a 10-g soil sample suspended in 10 mL of DI water while stirring on a magnetic stir plate until the pH reached 4.5. Suspension pH was measured with a pH electrode before each acid addition (i.e., after 20 min of stirring and equilibration). Data from the pH titration curves were used to calculate the equivalents of acid necessary for adjusting 200 g of each soil to reach a target pH of 7.5, 7.0, 6.5, 6.0, 5.5, and 5.0 for the soil acidification treatments.

Acid additions were separated into two different treatments: single-point acid addition in which all acid required to reach the target pH was added at the initiation of the incubation; and gradual acidification in which the same total amount of acid was split into eight different applications (one per week for 8 wk). For both acid treatments, 200 g of soil was placed in plastic cups (after being air dried and sieved to 2 mm) and mixed with the appropriate amount of acid in a volume of DI water that would result in 25% (w/w) moisture content. Each target pH (7, including an unamended control) was replicated three times for a total of 21 observational units for each soil and acid treatment (single-point acidification and gradual acidification).

During the first week of incubation, all soils were allowed to dry. Each soil was then thoroughly mixed to ensure that the previously added acid was mixed throughout. Soils were then brought back up to 25% moisture; from that point until the cessation of the incubation, the single-point acid addition soils were simply maintained at the 25% moisture level. On a weekly basis, the gradual acid addition soils were also brought up to 25% moisture, the difference being that the proper amount of acid was additionally mixed into the DI water used to maintain moisture.

After 8 total wk of incubation, all soils were air dried and mixed in preparation for analysis. Each soil was analyzed for WSP, M3-P, and pH as described above. Based on the results of that analysis (opposite trends for the WSP vs. pH relationship depending on acidification timing), soils were placed back into cups and incubated at 25% moisture content (no acid addition) for an additional 2 wk. At the end of the additional 2 wk (10 wk total), soils were again air dried and mixed in preparation for the same analyses.

## RESULTS AND DISCUSSION

### Background Soil Properties

Soils 1 and 2 are considered "excessive" in terms of soil test P as estimated by Mehlich-3 extract (Table 1), compared with optimum agronomic M3-P levels of 50 mg P kg<sup>-1</sup> (Beegle, 2002). These soil M3-P values also greatly exceed environmental P threshold values of 150 mg kg<sup>-1</sup>, as recommended by Sims et al. (2002). Due to high soil

**Table 1. Background properties of soils used in the acidification experiment.**

Soil	P†	Ca	K	Mg	P <sub>ox</sub> /(Al <sub>ox</sub> + Fe <sub>ox</sub> )‡	P <sub>M3</sub> /(Al <sub>M3</sub> + Fe <sub>M3</sub> )‡	CECS	pH	Sand	Silt	Clay	Organic matter
	mg kg <sup>-1</sup>						cmol <sub>c</sub> kg <sup>-1</sup>				%	
1	932	4389	1858	932	1.45	3.03	27.5	8.2	39.8	46.5	13.7	5.4
2	846	4366	2065	870	1.52	4.21	27.5	7.6	29.0	50.2	20.9	6.3

† Mehlich-3 extractable P, Ca, K, and Mg.

‡ Calculated from molar concentrations; ox = ammonium oxalate extractable with use of 0.5α value; M3 = Mehlich-3 extractable.

§ Cation exchange capacity.

P values, these soils clearly represent a potential P source to surface waters. Both soils have a loam texture and are similar in Mehlich-3 extractable Ca, K, and Mg concentrations (Table 1).

Soil pH (8.2 and 7.8 for Soils 1 and 2, respectively) was higher than expected for typical noncalcareous soils of Pennsylvania. Higher than normal organic matter contents, pH, and extractable P, Ca, K, and Mg (Table 1) also indicated that these soils have been impacted by the continuous addition of dairy manure. The high pH combined with unusually high M3-P and Ca values suggested that these soils may contain Ca-P. Dairy manure typically has a pH >7.0 (Chaubey et al., 1994; Sharpley and Moyer, 2000; Kleinman et al., 2002; Moller et al., 2002), which supports stable Ca-P minerals. The presence of Ca-P in dairy manure and the subsequent accumulation of Ca-P in soils receiving dairy manure can be explained by the large amounts of Ca-P supplemented to the animals' diet in the form of dicalcium phosphate and defluorinated phosphate (Wu and Ishler, 2002; National Research Council, 1998) and added Ca and Mg in the forms of dolomitic limestone and MgO, resulting in a pH >7.0.

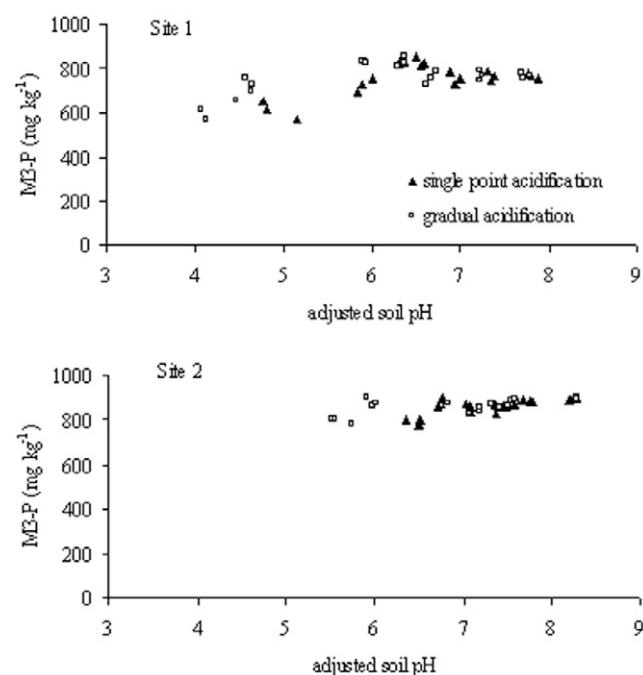
Further evidence for the accumulation of Ca-P is found in the MINTEQA2 speciation modeling data and the results of the sequential P fractionation. Using solution parameters obtained from the 1:5 soil/solution saturated paste extraction, MINTEQA2 predicted the

presence of hydroxyapatite in both soils. In addition, P concentrations within the bicarbonate- and acid-extractable (1.0 mol L<sup>-1</sup> HCl) P pools of the Hedley fractionation, considered to represent loosely bound P and Ca-P, were similar to those of manure-impacted, Ca-P-rich soils described by Sharpley et al. (2004). Soil 1 contained bicarbonate- and acid-extractable P concentrations of 434 and 175 mg P kg<sup>-1</sup>, respectively, while Soil 2 had 514 and 255 mg P kg<sup>-1</sup>, respectively. For comparison, unamended check soils of Sharpley et al. (2004) contained bicarbonate- and acid-extractable P concentrations of 26 to 103 and 7 to 99 mg P kg<sup>-1</sup>, respectively. Among alkaline soils such as those used in this study, the bicarbonate-extractable P pool of the Hedley fractionation is considered to remove a significant portion of the Ca-P pool through precipitation of Ca as CaCO<sub>3</sub>, thus releasing P bound with Ca (Kuo, 1996). Bicarbonate- plus acid-extractable P was 49 and 57% (percentage of the sum of all fractions) for Soils 1 and 2, respectively.

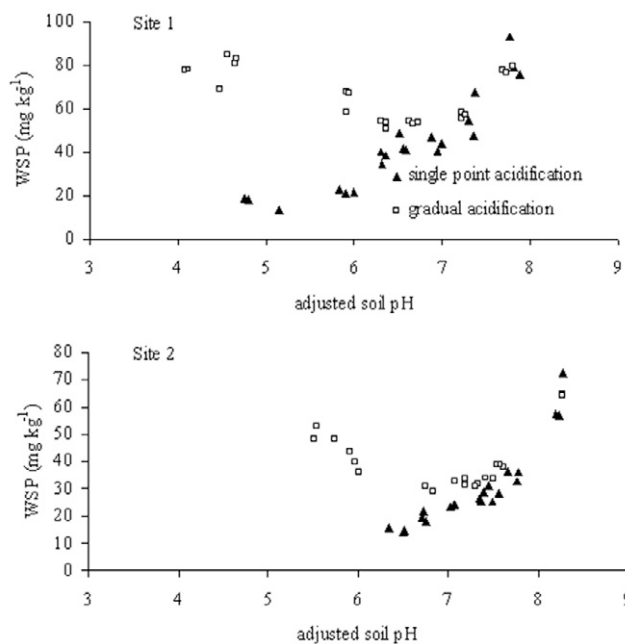
### Acidification of Calcium Phosphate Dominated Soils: Gradual Acidification vs. Immediate Acidification

The plots shown in Fig. 1 indicate that soil M3-P concentrations do not appear to be strongly influenced by the timing of acidification or pH. In other words, the relationship between soil M3-P and pH is similar for single-point acid addition and gradual acid addition. This observation can be explained by the strength of the Mehlich-3 extraction solution and its ability to extract various weakly bound P forms; i.e., Mehlich-3 is efficient at extracting weakly bound Al-related P, Fe-related P, and Ca-P. Consequently, although soil P forms may change in response to changing pH or acidification timing, the Mehlich-3 solution is still able to extract nearly the same amount of P.

In contrast, WSP is much more sensitive to changes in P form in response to changing pH and acidification timing. Acidification timing had a strong effect on the relationship between pH and WSP concentrations (Fig. 2). Adding all the acid in a single application at the initiation of the 8-wk incubation period (single-point acidification) resulted in a linear decrease in WSP with decreasing pH. This decrease in WSP with pH can be explained by dissolution of Ca-P and subsequent resorption onto soil Al and Fe minerals, which tend to be less soluble than Ca-P at a pH <7.0. Interestingly, addition of the same amount of acid spread out over the 8-wk incubation period (gradual acidification) resulted in a very different relationship between soil WSP and pH (Fig. 2). Under gradual acidification, WSP decreased with pH to a pH level of about 6.3 to 6.8, and then began to increase with further decreases in pH. In fact, the shape of the pH vs. WSP line for the gradual acidification treatment in Fig. 2 is very similar to solubility diagrams (pH vs. solution P) for pure Ca-P minerals such as dicalcium phosphate and octacalcium phosphate (Lindsay, 1979). From that perspective, the decrease in WSP from pH 8.3 to pH 7.0 is a result of calcite dissolution, providing more Ca in solution for reaction with P, and the increase in WSP in response to



**Fig. 1. Effect of soil pH and rate of pH adjustment on soil Mehlich 3-P (M3-P) concentrations for Sites 1 and 2 after 8-wk incubation. Single-point acidification = all acid added at incubation initiation; gradual acidification = acid applied in eight increments (one application per week).**

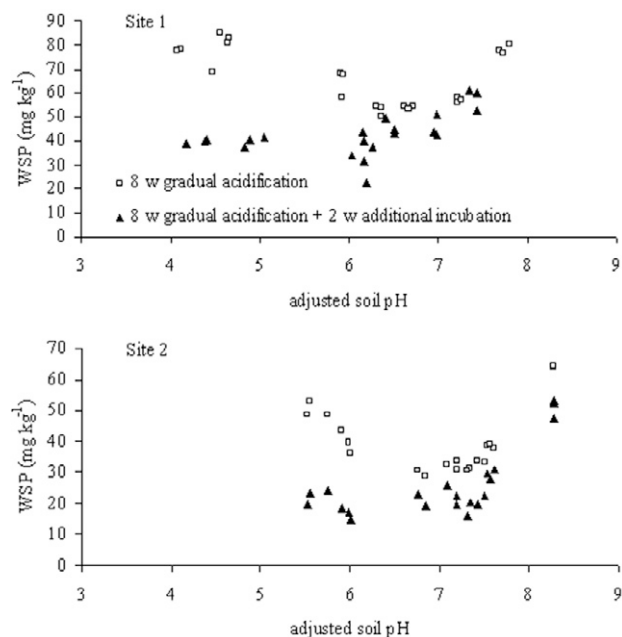


**Fig. 2.** Effect of soil pH and rate of pH adjustment on soil water-soluble P (WSP) concentrations for Sites 1 and 2 after 8-wk incubation. Single-point acidification = all acid added at incubation initiation; gradual acidification = acid applied in eight increments (one application per week).

acidification below pH 6.7 is due to the inherent solubility of Ca-P (Lindsay, 1979).

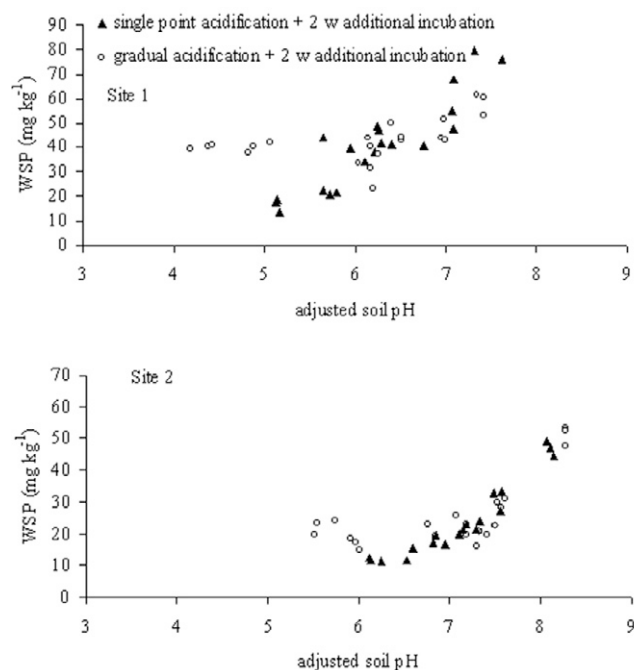
One possible explanation for the observed behavior following gradual acidification is that soluble P from dissolving Ca-P has not been resorbed onto soil Al and Fe minerals within the 2-wk incubation period following the last acid addition. Further evidence for this explanation is shown in Fig. 3 and 4. When the soils treated with gradual acidification were allowed to incubate for an additional 2 wk without further acid additions (Fig. 3), WSP concentrations in the soils with pH <7.0 decreased. The resulting WSP concentrations following gradual acidification after two additional weeks of incubation (10-wk total) were similar to those for single-point acidification after the 10-wk incubation (Fig. 4).

Similar to the results of single-point acidification, Scheinost and Schwertmann (1995) observed the effect of pH on soil adsorption-desorption among 2448 noncalcareous German soil samples. They found that P adsorption was negatively correlated to pH in the range of 4 to 6.5 and positively correlated in the range of 6.5 to 7.5. In another study involving noncalcareous soils, De Smet et al. (1998) related soil properties to P release from 888 soils from Belgium. Results indicated that P desorption rates increased with increasing pH from 3.75 to 6.5. Among calcareous soils, Zhang et al. (2004) found that N fertilization via  $\text{NH}_4^+$  [ $(\text{NH}_4)_2\text{SO}_4$ ] decreased the rhizosphere pH of wheat (*Triticum aestivum* L.) by 0.30 to 0.65 units. This acidification resulted in increased P uptake by the plant due to dissolution of Ca-bound phosphates. Nitrogen applications in the form of  $\text{NO}_3^-$  ( $\text{KNO}_3$ ) had less of an impact on soil inorganic P fractions. The unique aspect of the findings of this study is the development of a Ca-P-dominated soil among typically acidic eastern U.S. soils. These soils are generally dominated by Fe- and Al-related P; conversion to a Ca-P-dominated system through years of excessive animal manure additions allowed WSP concentrations to remain higher than if the soil P chemistry was Al and Fe based and acidic. The important issue



**Fig. 3.** Relationship between soil pH and water-soluble P (WSP) among soils gradually acidified compared with the same soils incubated for 2 more wk without receiving any additional acidification.

in this case is in regard to the fate of the soluble P produced as Ca-P dissolves with decreasing pH. Results indicated that acidification of such soils could benefit water quality by eventually decreasing WSP concentrations. Acidification of these Ca-P soils, however, may result in a temporary spike in WSP concentrations until the newly dissolved Ca-P (i.e., the cause of a WSP spike) re-equilibrates with soil Fe and Al. This data set cannot determine if such a phenomenon occurred immediately on acidification; a future study could address this question.



**Fig. 4.** Relationship between soil pH and soil water-soluble P (WSP) concentrations for Sites 1 and 2 soils treated with a single-point acidification (all acid added at incubation initiation) and gradual acidification (acid applied in eight increments, one application per week) following 2 wk of additional incubation (10 wk total).



## Practical Aspects of Acidification of High Calcium Phosphate Soils

From a practical perspective, the acidification that eventually resulted in a net decrease in soil WSP concentrations among heavily manured Ca-P-rich soils is probably dependent on certain soil properties, the most obvious of which is the amount of soil Ca-P and the ratio of Ca-P to reactive Al + Fe. The eventual net decrease of soil WSP would be dependent on soil Al and Fe contents in addition to the P saturation status of soil Al and Fe. If there were very little reactive Al and Fe for the dissolved Ca-P to resorb to, then any potential WSP decrease on acidification may be insignificant or nonexistent. In this study, the soils contained ammonium oxalate extractable Al + Fe (considered highly reactive with P) concentrations from 3000 to 3500 mg kg<sup>-1</sup>, which was obviously sufficient for resorbing the dissolved Ca-P. A worst-case scenario (for P loss potential to surface waters) would be acidification of a soil rich in Ca-P with very little reactive Al and Fe. In that case, acidification might result in a more permanent increase in WSP. The aforementioned worst-case scenario may pertain to a relatively few coarse-textured soils with a highly siliceous mineralogy. Loamy soils with mixed mineralogy, such as those used in this study, however, should typically contain pools of potentially reactive Al and Fe sufficient to bind P that is released by Ca-P dissolution.

Due to recently approved regulations and the prediction of further future limitations on the application of animal wastes to high-P soils in areas such as the Chesapeake Bay and Eucha-Spavinaw watersheds (Simpson, 1998; Haggard et al., 2005), soils with long histories of manure applications (probably with high Ca-P) will slowly acidify unless they are limed. Sato et al. (2005) suggested that a pH decrease due to a reduction or elimination of poultry litter additions to heavily poultry-litter-amended soils high in Ca-P would increase the solubility of Ca-bonded inorganic P minerals, and concluded that "maintaining a high pH is therefore an important strategy to minimize P leaching in these soils." The results of this study suggests that depending on soil properties and acidification timing, acidification of such soils can result in lower long-term WSP concentrations, therefore posing less risk for contributing soluble P to leachate or runoff.

Due to the fact that the acidification experiment was conducted using only two similar soils, it is difficult to extrapolate our results to all heavily manured soils. Therefore, further research is required to determine if the results of this study represent a relatively unique phenomenon or something to be expected from many soils with a long-term history of excessive manure applications.

## CONCLUSIONS

Acidification of heavily manured, Ca-P-dominated soils resulted in a decrease in WSP concentrations since sufficient unsaturated (with respect to P) Al and Fe were present such that dissolved Ca-P sorbed to Al and Fe. The eventual decrease in soil WSP concentrations resulting from acidification is a benefit with regard to water quality and prevention of nonpoint losses of dissolved P from soils to surface waters. Changes in WSP following acidification were probably dependent on the amount of reactive Al and Fe, the amount of P bound with Ca, the extent of acidification, and the kinetics of the acidification, dissolution, and resorption reactions. These changes in WSP may influence the risk of soluble P losses in leachate or runoff. Further research is necessary to determine if acidification of other Ca-P-dominated (from excessive manure applications) soils has a strong influence on soil WSP concentrations, and if so, what effect might typical agricultural

management practices (fertilizer applications, cessation of manure application) have on the degree and kinetics in which it occurs.

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